

Microstructural Development from Electron Microscopy

- Microstructural development in ex-situ BaF_2 YBCO films.
 - ✓ Laminar vs. columnar structures
 - ✓ PVD- BaF_2 and MOD- BaF_2 ex-situ films
 - ✓ The role of liquid phases in phase development
- Current limiting microstructures
- The “porous microstructure”
- Wrapup



PVD- BaF_2 : Physical vapor deposition of precursors



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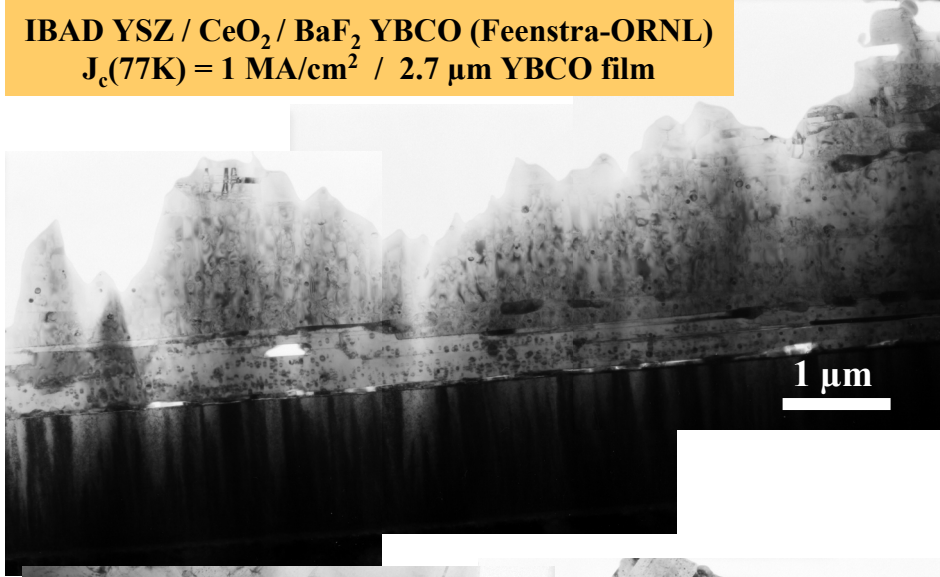


MOD- BaF_2 : Metal organic deposition of precursors

High current YBCO coated conductors can have different film morphologies that are process dependent.

- Laminar vs. columnar growth (Does it matter??)
- Laminar growth is characteristic of the MOD and PVD-BaF₂ conversion processes.

IBAD YSZ / CeO₂ / BaF₂ YBCO (Feenstra-ORNL)
 $J_c(77K) = 1 \text{ MA/cm}^2$ / 2.7 μm YBCO film



IBAD YSZ / CeO₂ / PLD YBCO (Foltyn-LANL)
 $J_c(75K) = 1.7 \text{ MA/cm}^2$ / 1.5 μm YBCO film



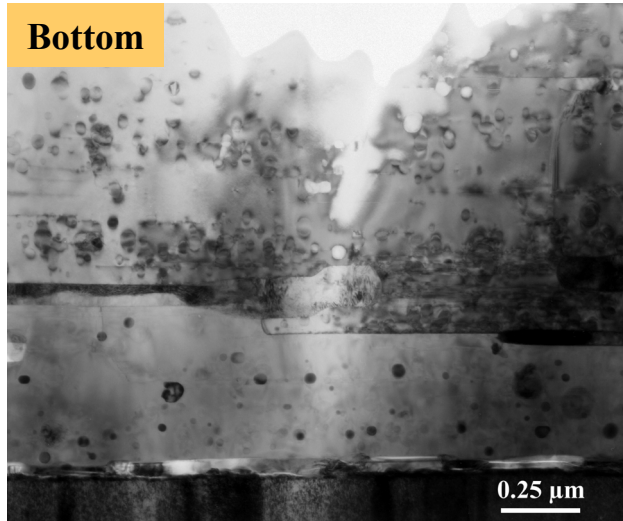
MOD YBCO / CeO₂ / YSZ / Y₂O₃ / Ni / NiW RABiTS™
0.84 μm YBCO $J_c(77K) = 2.0 \text{ MA/cm}^2$ (Rupich - AMSC)



The “standard” conversion of PVD-BaF₂ YBCO films on IBAD YSZ templates produced high-J_c films with a bi-modal microstructure.

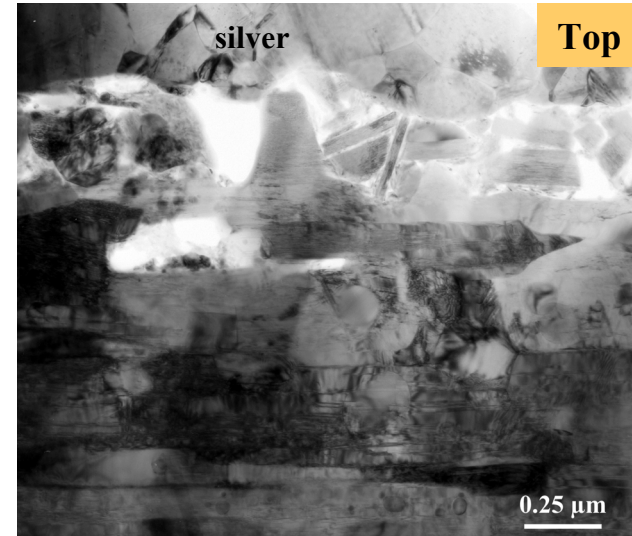
- **Bi-modal:** Large, well formed, low J_c YBCO grains in bottom half of film and smaller, faulted YBCO grains in the top half.
- Two different growth modes indicated by different grain morphologies and phase assemblages.

IBAD YSZ (LANL) / CeO₂ / BaF₂ YBCO (ORNL)
J_c(77K) = 1 MA/cm² / 2.7 μm YBCO film / 270 A/cm-width



Large, low-J_c YBCO grains (> 10 μm)

Y₂O₃ precipitates, large Ba-Cu-O
secondary phases, minor amounts
YCuO₂, CuO.

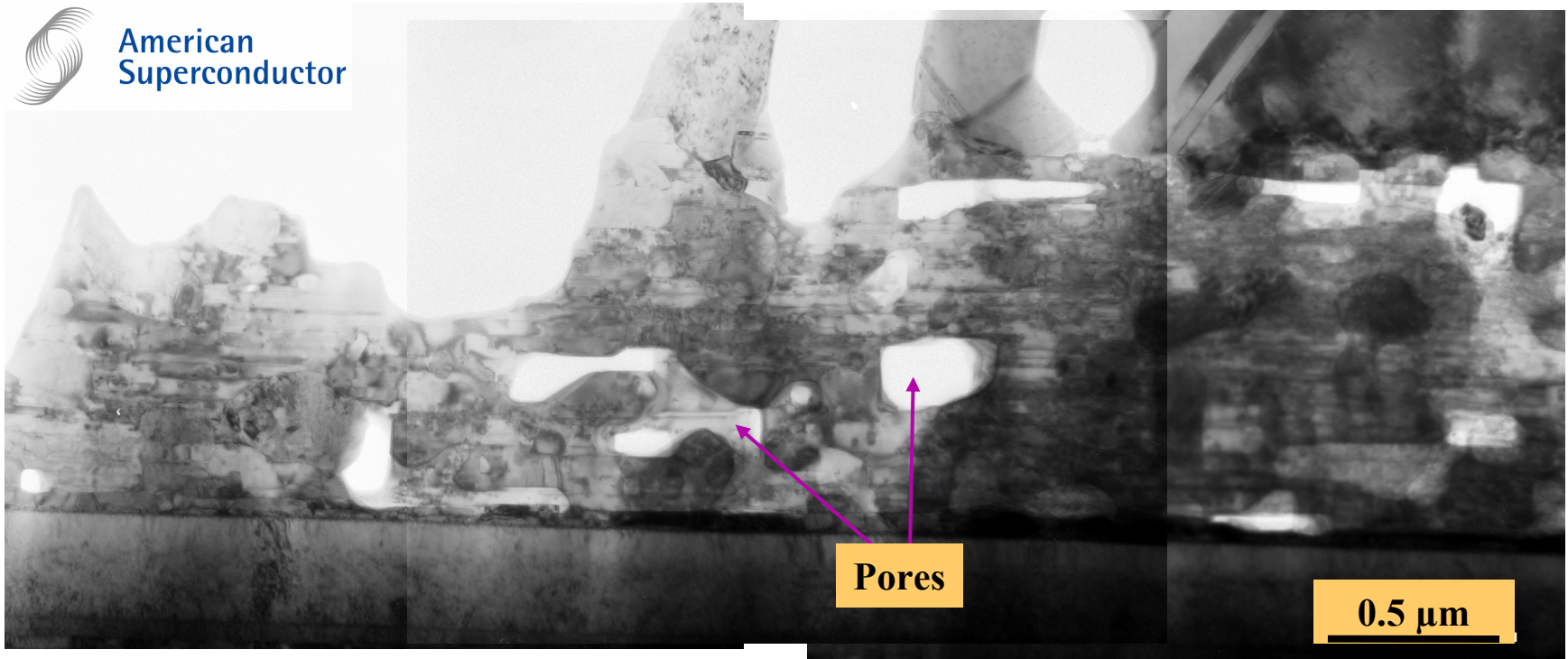


Small YBCO grains

Multiple secondary phases
YCuO₂, Y₂O₃, Ba₂Cu₃O_y, and BaCu₂O_y

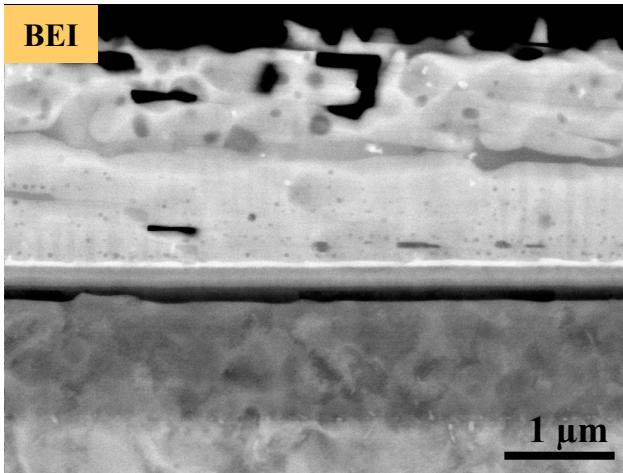
The ex-situ conversion of MOD-BaF₂ YBCO precursors on RABiTS produced very high J_c films that did not have a bi-modal structure.

- 0.8 μm YBCO / CeO₂ / YSZ / Y₂O₃ / Ni / NiW (RABiTS)
 - ✓ I_c = 270A/cm width. (Full width measurement!)
 - ✓ J_c ≈ 3.4 MA/cm² (≈0.8 μm YBCO)
- “porous microstructure” - small-grain, faulted YBCO structure that is uniform thru thickness in spite of all the porosity.



The “standard” ex-situ conversion of PVD-BaF₂ films on RABiTS™ produced the bi-modal structure over a wide range of film thicknesses.

2.1 μm $J_c = 0.44 \text{ MA/cm}^2$ $I_c = 93 \text{ A/cm-width}$



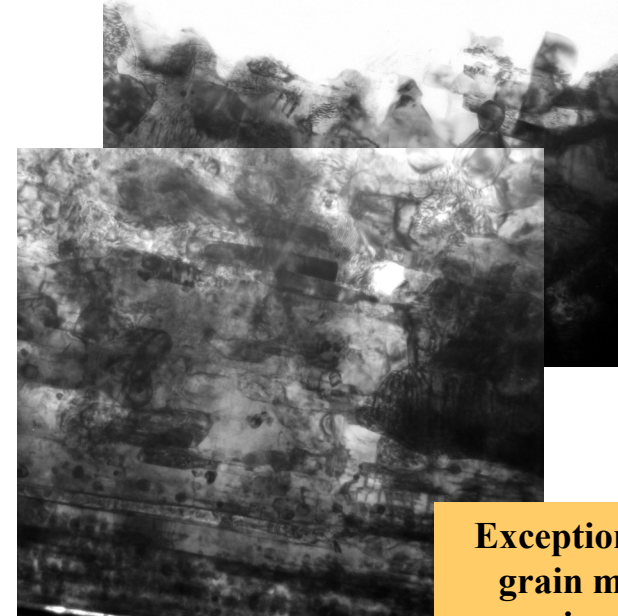
→ The bi-modal structure is process, not substrate, dependent.

→ Rule-of-thumb: Large grain material comprises ≈ 1/2 of the film thickness.

Small-grain
YBCO

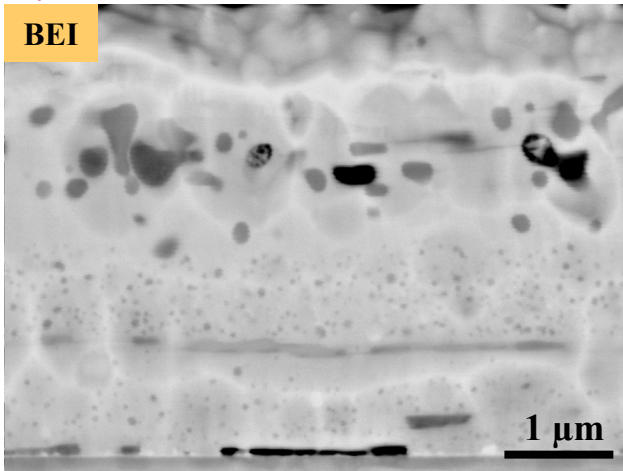
Large-grain
YBCO
Buffer layers
NiO

Ni



Exception: Large grain material comprises less than half of the film.

5 μm $J_c = 0.31 \text{ MA/cm}^2$ $I_c = 155 \text{ A/cm-width}$

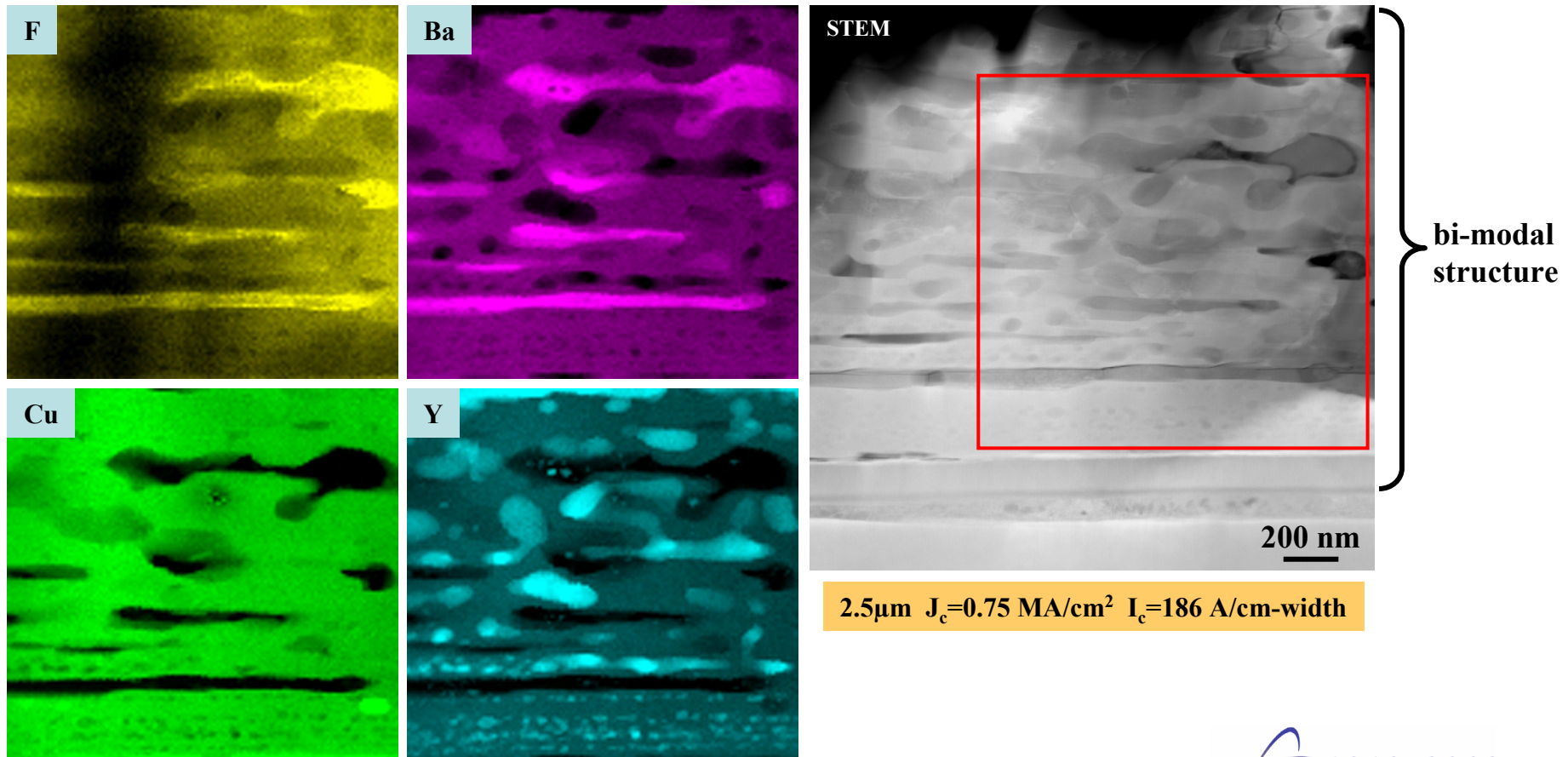


0.5 μm

2.5 μm $J_c = 0.75 \text{ MA/cm}^2$ $I_c = 186 \text{ A/cm-width}$

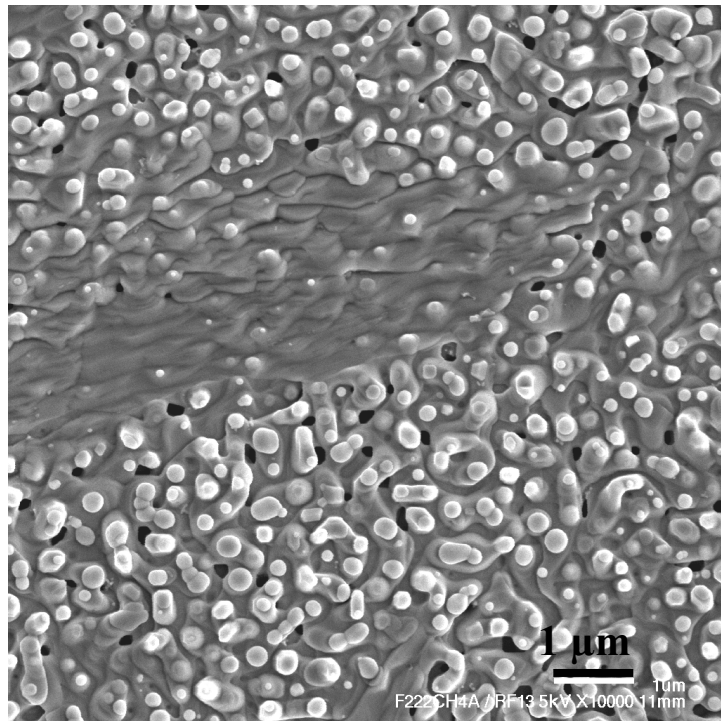
The bi-modal structure is a process dependent structure derived from the presence of excessive amounts of liquid phases during conversion.

- Remnants of the liquid phase (Ba-O-F) can be found in some of the fully processed films.
- Typically, the Ba-Cu-O phase takes the place of the Ba-O-F.
- Spectral images (below) show the distribution and extent of the secondary phases.

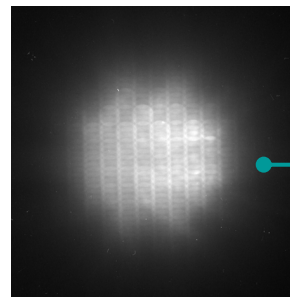


Too much liquid phase during processing can also cause the formation of YBCO colonies tilted out-of-plane.

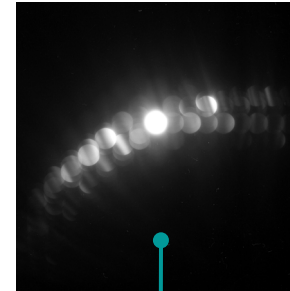
- Colonies of tilted grains (not a-axis) can form above layers of liquid phase; their intersections with the film surface are easily viewed by SEM.
- Tilted grains can have both out-of-plane and twist components.



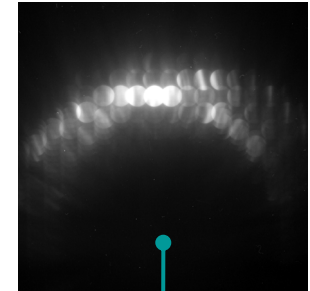
YBCO on zone axis



Out of plane tilt with a twist component.



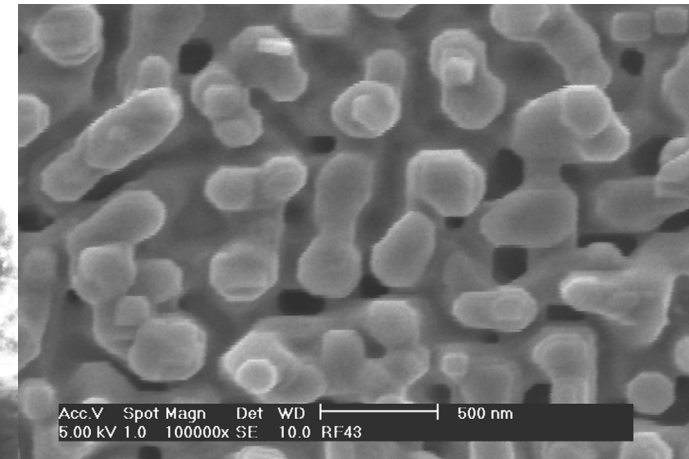
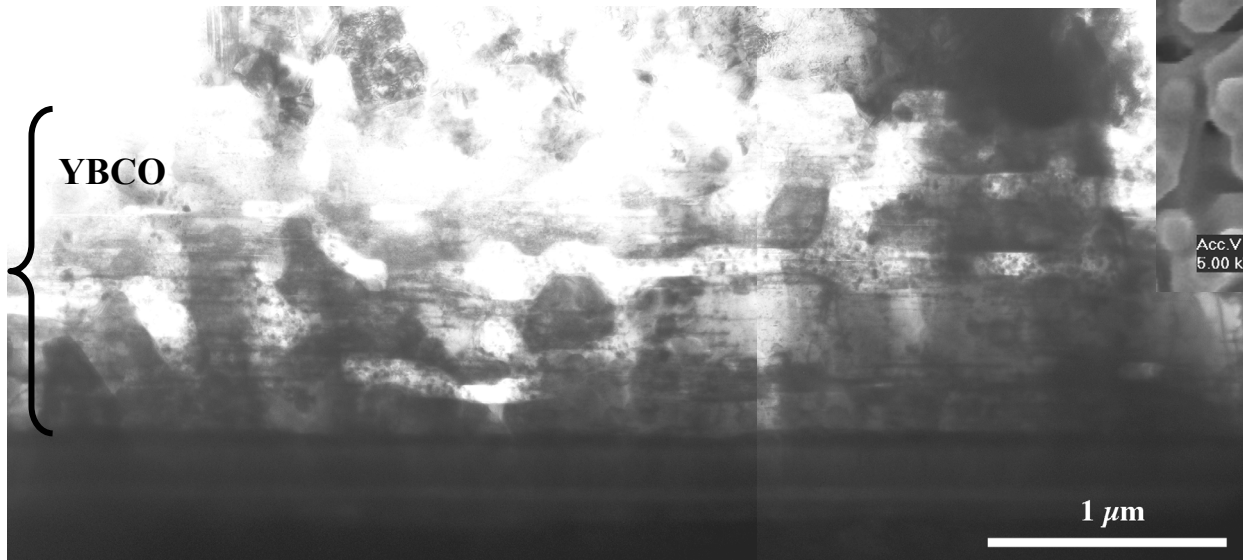
Out of plane tilt



IBAD YSZ / CeO_2 / BaF_2 YBCO (Feenstra-ORNL)
 $J_c(77\text{K}) = 0.9\text{-}1 \text{ MA/cm}^2$ / 2.7 μm YBCO film

A “champion” PVD-BaF₂ film on RABiTS™ did not contain the bi-modal structure.

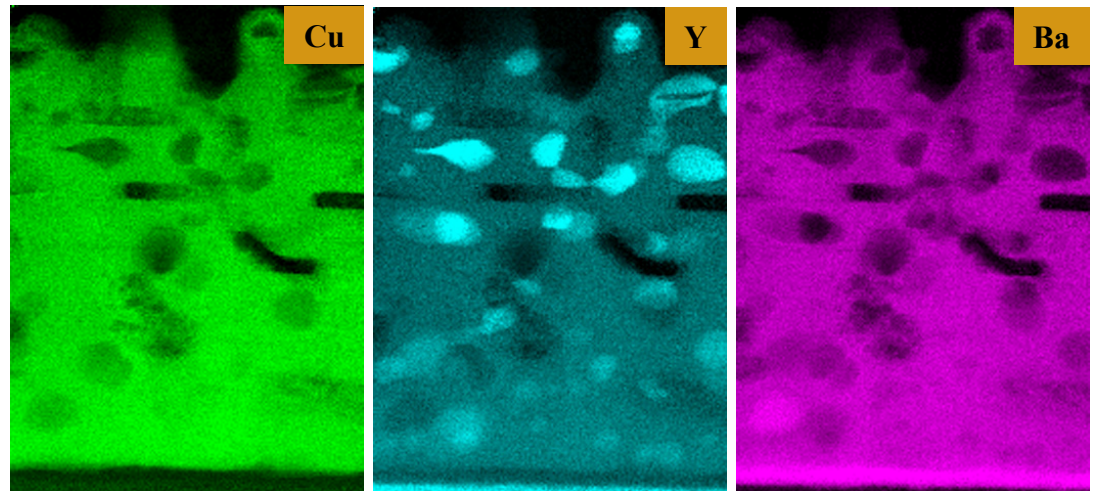
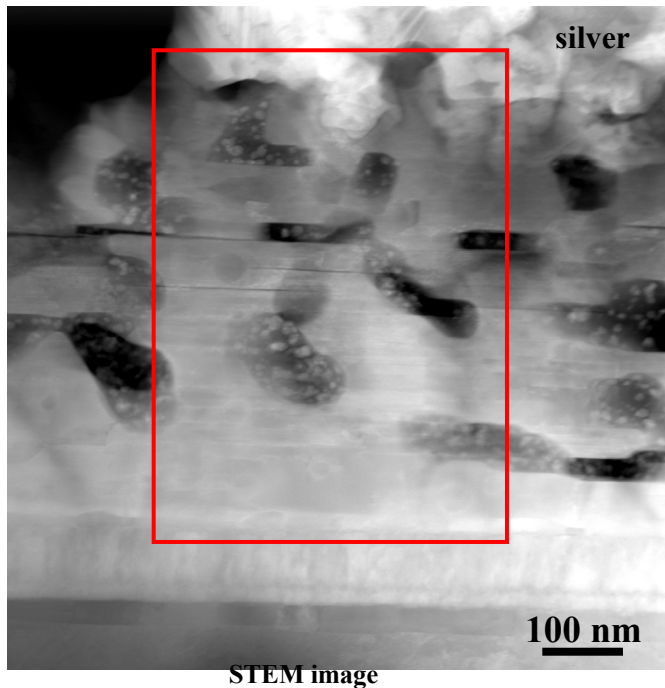
- 1.35μm YBCO $J_c = 1.69 \text{ MA/cm}^2$; $I_c = 228 \text{ A/cm-width}$
- An exception to the norm in the “standard processing” provided insight into how the microstructure and superconducting properties can be improved.
- The high- J_c “porous microstructure” can be obtained from a PVD-BaF₂ conversion process.



YBCO / CeO₂ / YSZ / Y₂O₃ / Ni / NiW

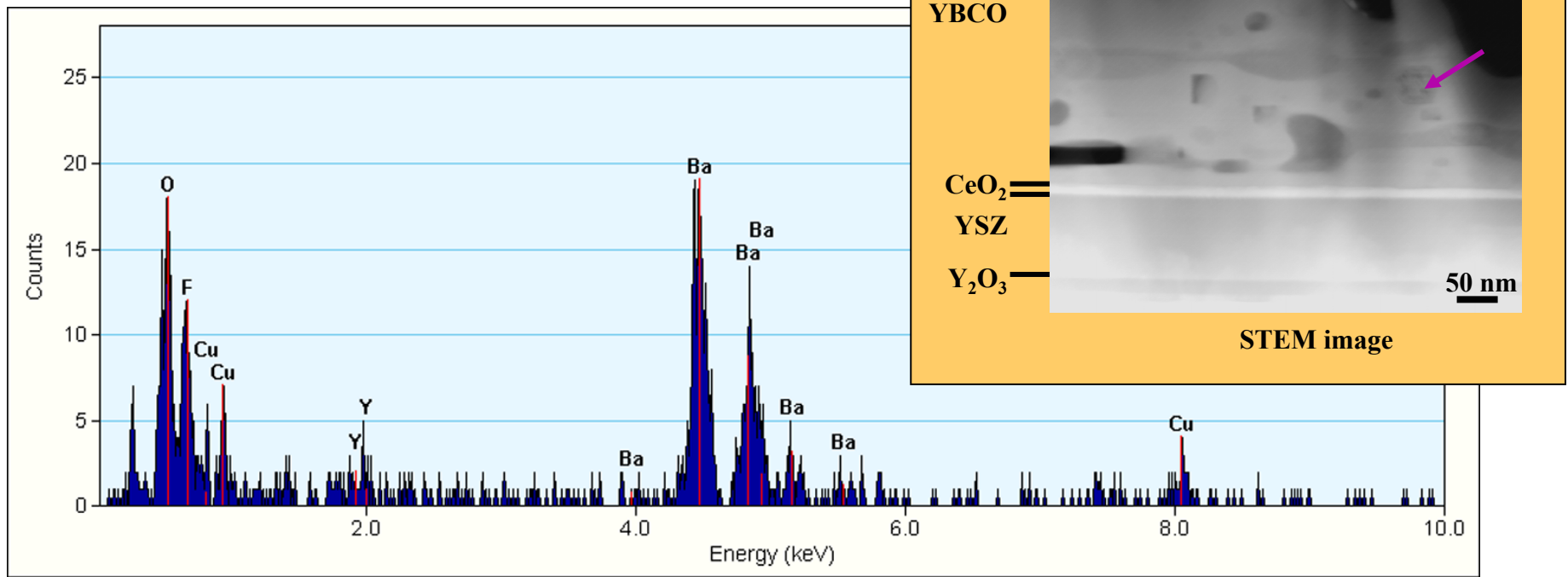
The microstructure and phase assemblage of the “champion” PVD-BaF₂ sample suggested a reduced amount of liquid phase during conversion.

- Spectral imaging shows a uniform distribution of secondary phases within the porous microstructure.
- ✓ Very few, large Ba-Cu-O phases
 - ✓ Very few Y₂O₃ precipitates within grains
 - ✓ Random mix of “round” Y₂O₃, YCuO₂, and Ba-Cu-O phases



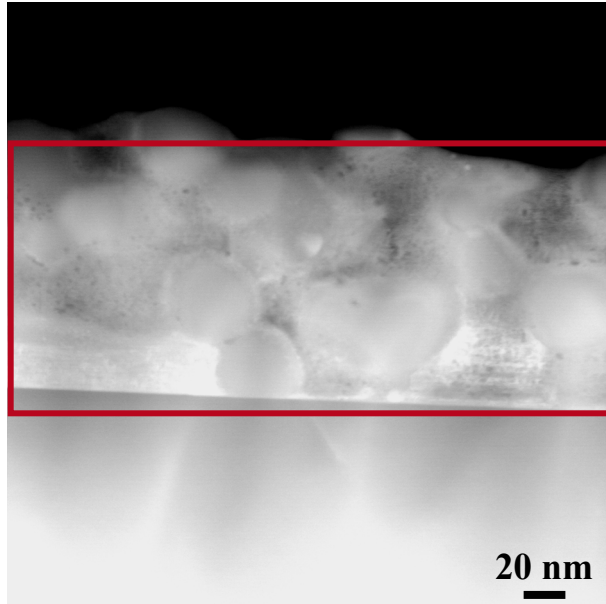
Residual fluorine was found in the high- J_c (3.4 MA/cm²) AMSC MOD-BaF₂ YBCO coated conductor.

- ➔ Not necessary to remove all F from the films. (shorter processing times!)
- ➔ Residual F (Ba-Cu-O-F or BaO_xF) suggests an important role for liquid phase assisted growth in the conversion process.



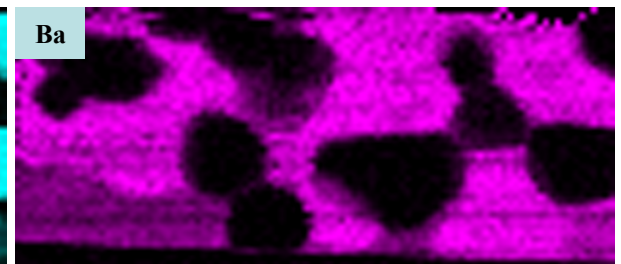
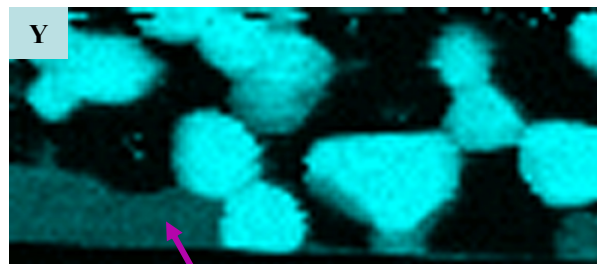
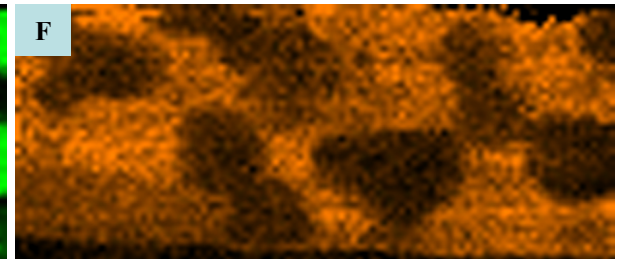
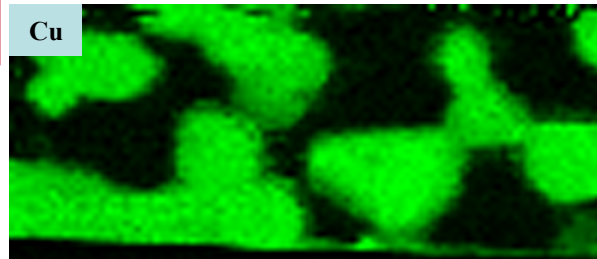
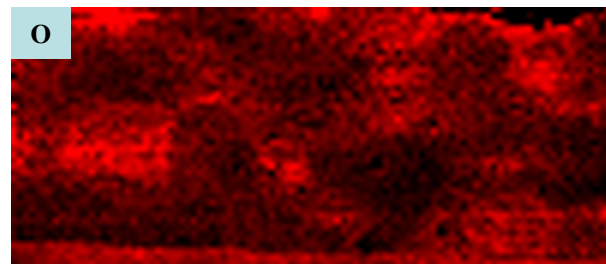
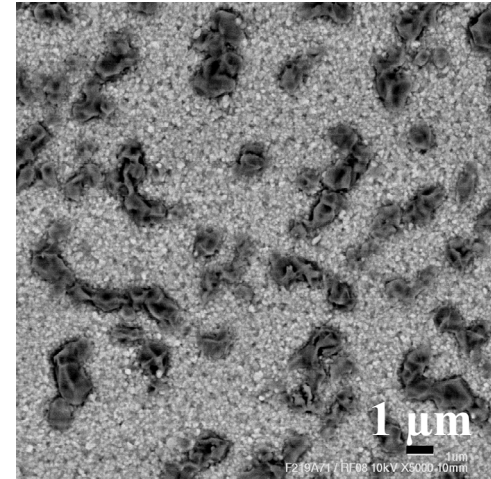
Understanding the role of the liquid phase in the *ex-situ* conversion of the BaF_2 precursors is a key area for obtaining a high- J_c microstructure.

- In the thin films, a segregation of the precursor into Ba-O-F (liquid phase?) and YCuO_x occurs. (what happens to the rest of the copper?)
- Laminar YBCO growth starts at the substrate interface.



SEM image - CuO segregation

0.3 μm precursor on (100) SrTiO_3
Quenched after 0.3 hours

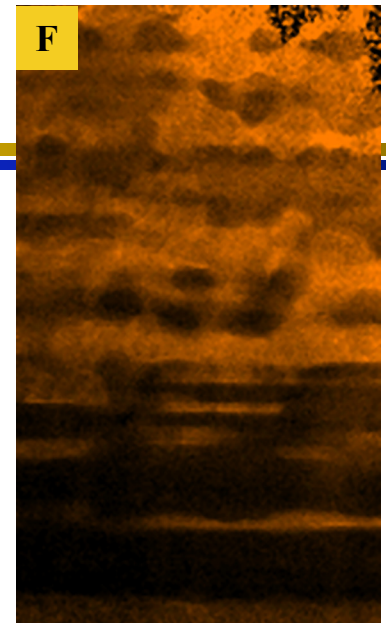
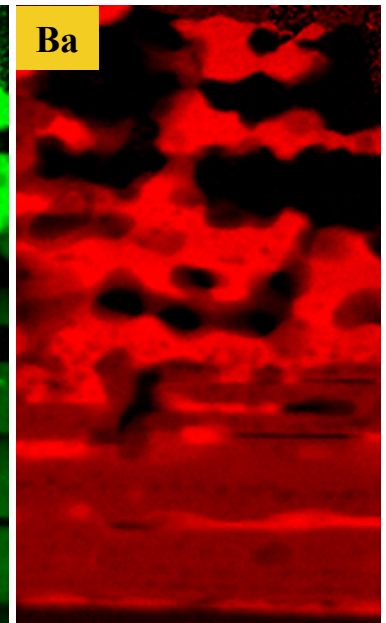
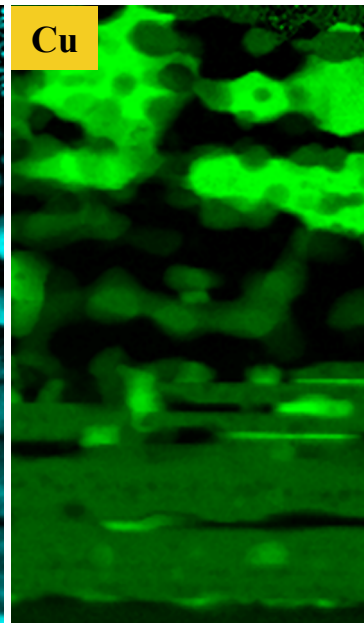
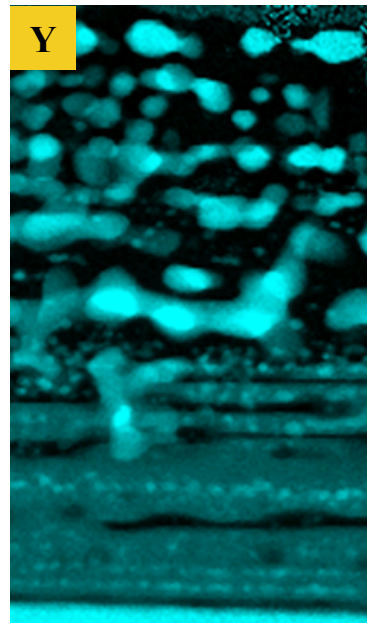
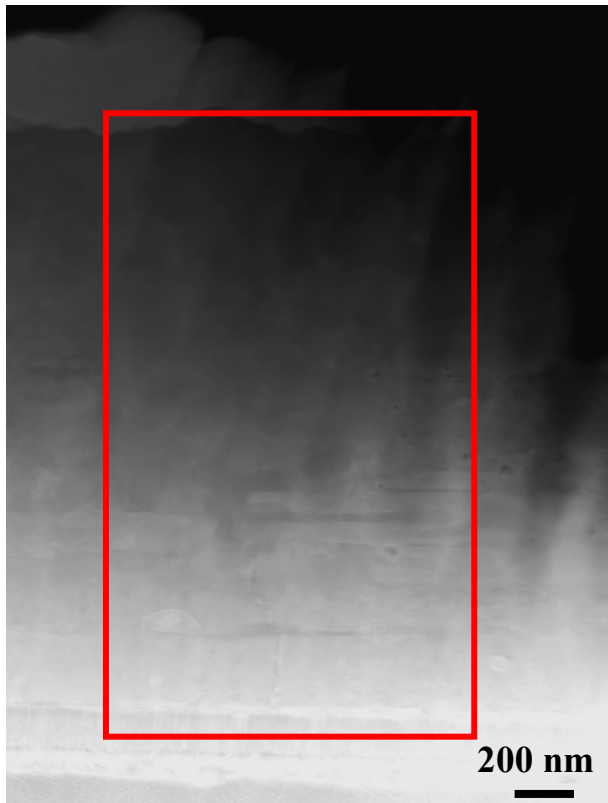


YBCO grain growing on the substrate.

The starting thickness of the precursor film also affects the conversion process.

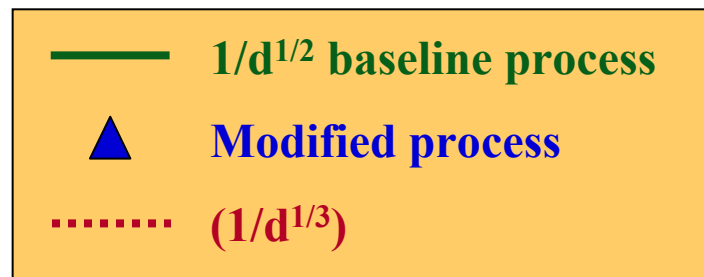
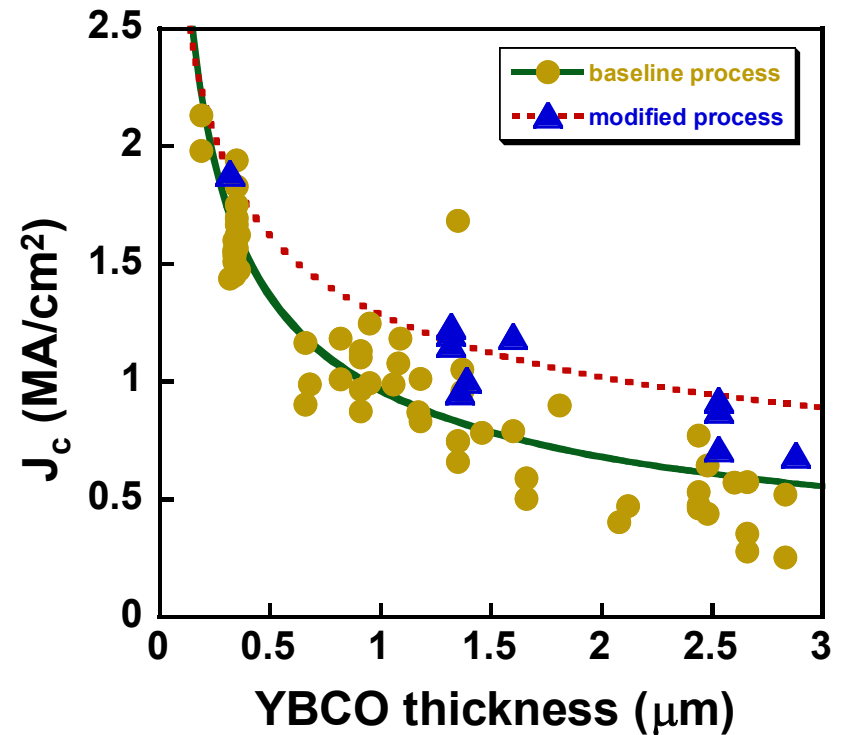
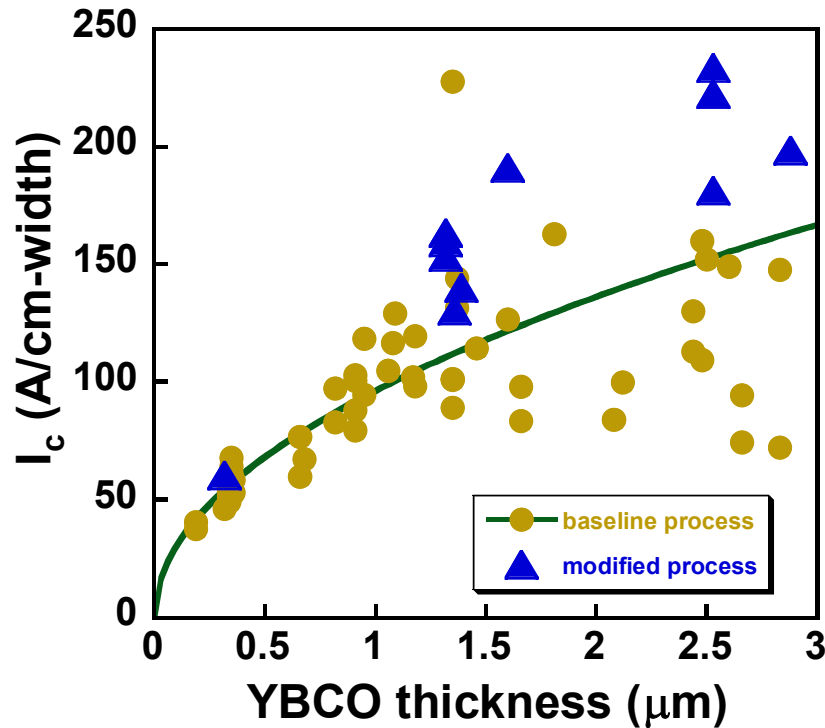
- CuO segregation
- Ba-O-F and YCuO_x again associated with precipitation of YBCO.
- Y_2O_3 particles floating in the Ba-O-F near growth front.
 - ✓ $(3) \text{YCuO}_x + (2) \text{Ba-O-F} \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_y + \text{Y}_2\text{O}_3$
 - ✓ Layered Y_2O_3 structure within the large YBCO grains.
- Start of small grain YBCO nucleation in top half of film.

2.66 μm film on RABiTS quenched after 1.5 hours total processing time

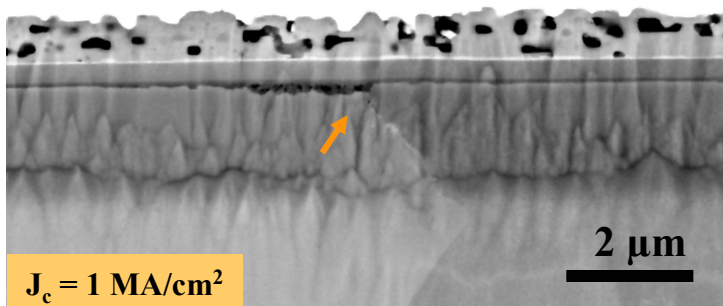
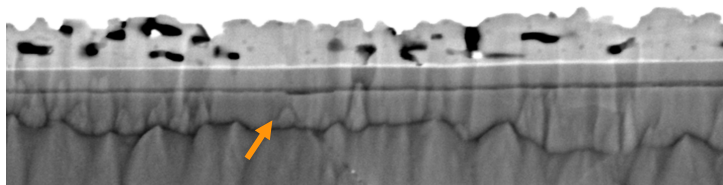
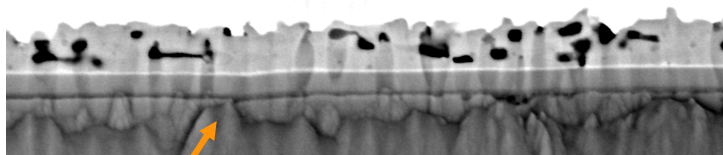
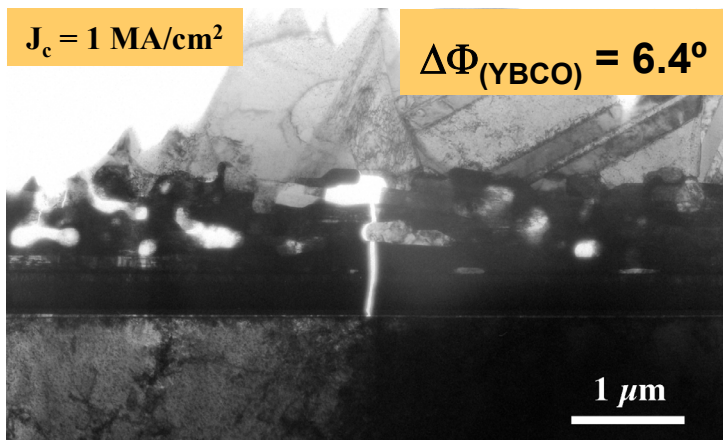


New process methodologies developed from microscopy and ion-milling insights resulted in improved transport properties for PVD-BaF₂ films.

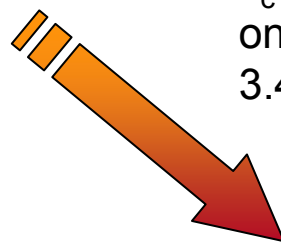
→ PVD-BaF₂ YBCO films of various thickness on RABiTS.



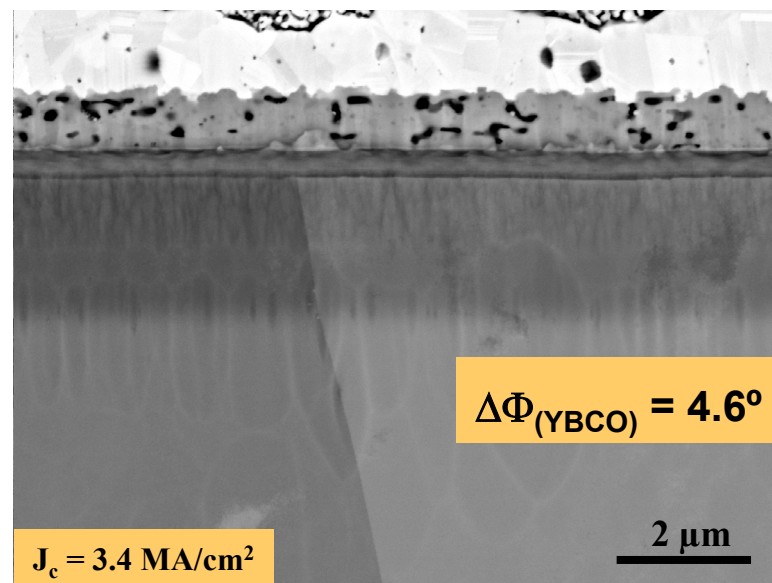
Control of the liquid phases is but one area for I_c improvement as evidenced by AMSC's recent advances in MOD-BaF₂ YBCO films on RABiTS.



- Cracks were observed in early AMSC MOD BaF₂ films.
- Early films also had non-planar surfaces and grain boundary grooving.
- J_c values for 0.8 μm MOD-BaF₂ YBCO films on RABiTS have been raised to the level of 3.4 MA/cm².



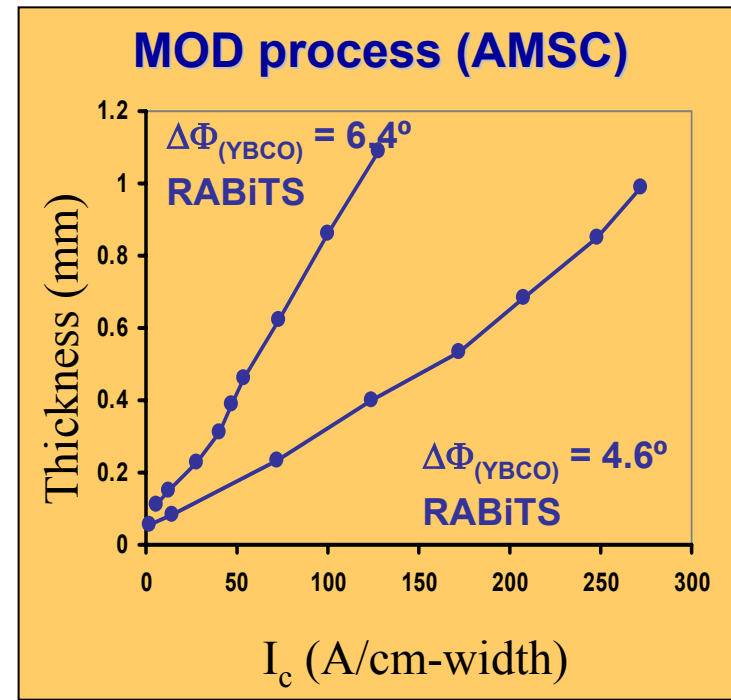
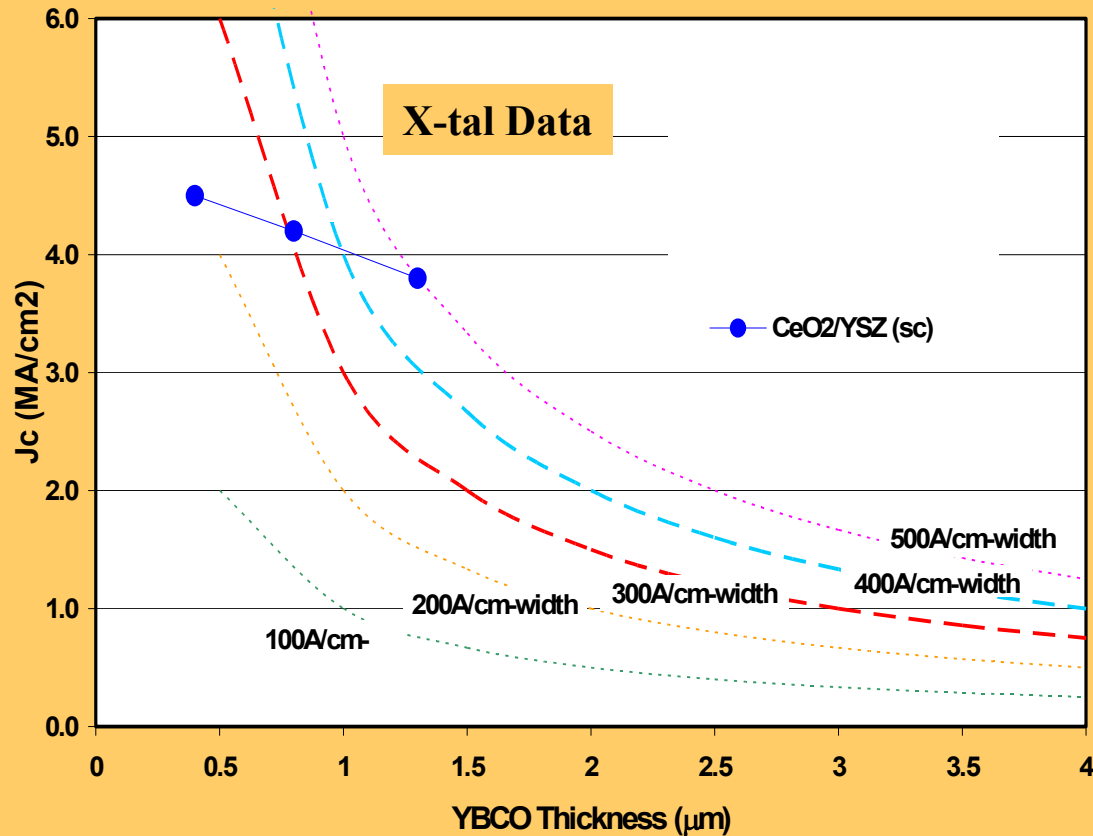
Process Improvement



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The “porous microstructure” is the structure associated with the high- J_c , ex-situ BaF_2 YBCO films.

- ? Better structure (minimal out-of-plane tilt)
- ? Better pinning by small, faulted YBCO grains
- ? Better flux pinning via increased surface area
- ? Formation of a pseudo multi-layer microstructure; periodicity determined by grain size



MOD BaF_2 YBCO / CeO₂ / SC YSZ

0.4 μm	$J_c = 4.4 \text{ MA/cm}^2$
0.8 μm	$J_c = 4.2 \text{ MA/cm}^2$
1.3 μm	$J_c = 3.8 \text{ MA/cm}^2$



FY2003 Results (Scoring Criterion)

→ Goal - Determine → Results

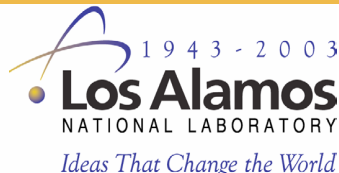
the dependence
of J_c on YBCO
film thickness.

- ✓ Films up to 3 μm thick on RABiTS, IBAD-YSZ, and x-tal YSZ
- ✓ Functional dependence of J_c on d is template independent
- ✓ Substrate (texture) controls level of J_c and I_c
- ✓ $J_c(d)$ of PVD-BaF₂ films with “standard” conversion conditions fitted to $J_c = J_\Phi * J(d)$ where J_Φ is texture dependent scaling factor and $J(d) = 1/d^{1/n}$ where $n=2$
- ✓ TEM correlations show a non-uniform structure in PVD-BaF₂ films suggesting an extrinsic dependence for $J_c(d)$
- ✓ Improved processing of PVD-BaF₂ films leads to higher J_c values and suggests a weaker $J_c(d)$ dependence.
- ✓ $J_c(t)$ dependence of homogeneous, 1 μm thick, MOD-BaF₂ films is almost linear in thickness contradicting the “intrinsic” model for point defect pinning.
- ✓ Absence of dead layers in ex-situ YBCO films.
- ✓ Linear $I_c(t)$ implies higher I_c 's for thicker YBCO films.

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FY2003 Results (Scoring Criterion)

→ Goal –Correlation → Results

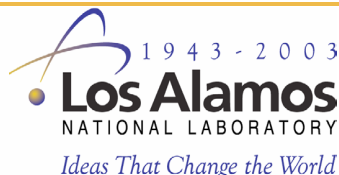
of the
microstructure
with the
superconducting
properties.

- ✓ Identified process dependent, laminar growth modes in the ex-situ conversion of BaF₂ films
 - Bi-modal structures
 - “porous microstructure”
- ✓ Identified current limiting structures in both PVD and MOD BaF₂ films
 - Tilted colonies
 - Cracks, grain boundary discontinuities
 - Bi-modal structure
- ✓ Showed relationship between the “porous microstructure” and high-J_c films.
 - MOD BaF₂ film J_c = 3.4 MA/cm²; 270 A/cm-width
 - PVD BaF₂ film J_c = 1.7 MA/cm²; 228 A/cm-width
- ✓ Constant J_c(t) typically observed from ion-milling, but doesn't necessarily reflect a homogenous microstructure.

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FY2003 Results (Scoring Criterion)

→ Goal - Understand the BaF_2 conversion process and develop methodologies for process improvement.

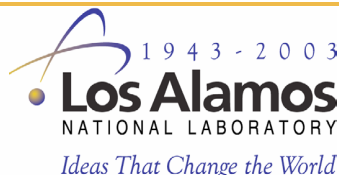
→ Results

- ✓ Identified the role of liquid phases in microstructural development
- ✓ Showed an early phase evolution of YCuO_x and Ba-O-F in thin films; deviations occur in the conversion of thicker films.
- ✓ Improved the PVD- BaF_2 processing with microstructural and ion milling J_c information.
- ✓ Faster conversion speeds obtained (3-7 Å/s)
- ✓ Showed that the “porous microstructure” can be obtained with both MOD- BaF_2 and PVD- BaF_2 .
- ✓ Showed that the size of the YBCO grains is independent of the substrate type (process dependent).

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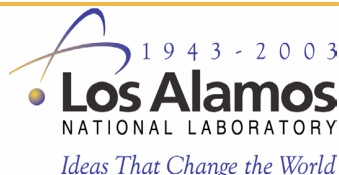
FY2003 Results (Scoring Criterion)

- | | |
|---|---|
| <p>→ Goal - Produce high current YBCO coated conductors with ex-situ conversion of PVD-BaF₂ based films.</p> | <p>→ Results</p> <ul style="list-style-type: none">✓ Showed that PVD-BaF₂ ex-situ conversions can produce the MOD-BaF₂, high-J_c “porous microstructure.”✓ Exceeded 200 A/cm-width for PVD-BaF₂ films on both IBAD YSZ and RABiTS.<ul style="list-style-type: none">● 1.4 μm 228 A/cm-width (“champion”)● 2.5 μm 233 A/cm-width (modified process)✓ Obtained J_c = 2 MA/cm² for thin PVD-BaF₂ film on an IBAD MgO template. |
|---|---|

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FY2003 Performance (Scoring Criterion)

- Goal - Determine the dependence of J_c on YBCO film thickness.
- Performance
 - ✓ Correlated the thickness dependence of J_c with spatially correlated, process dependent microstructure
 - variable thickness films
 - through-thickness J_c by ion milling
 - ✓ Intrinsic and extrinsic issues pertaining to $J_c(d)$ were identified
- Goal –Correlation of the microstructure with the superconducting properties.
- Performance
 - ✓ Identified process dependent laminar growth modes in the ex-situ conversion of BaF_2 films
 - ✓ Compared spatially correlated microstructural data with transport and ion milling data to understand potential current limiting mechanisms and to determine an optimal structure for ex-situ films.

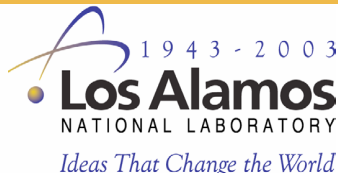
FY2003 Performance (Scoring Criterion)

- ➔ Goal - Understand the BaF_2 conversion process and develop methodologies for process improvement.
- ➔ Performance
 - ✓ Started the investigation of the role of liquid phases in microstructural development.
 - ✓ Developed improved PVD- BaF_2 processing routes using the microstructural and ion milling J_c information.
- ➔ Goal - Produce high current YBCO coated conductors with ex-situ conversion of PVD- BaF_2 based films.
- ➔ Performance
 - ✓ Exceeded 200 A/cm-width for PVD- BaF_2 films on both IBAD YSZ and RABiTS.
 - ✓ Obtained $J_c = 2 \text{ MA/cm}^2$ for thin PVD- BaF_2 film on an IBAD MgO template.
 - ✗ Unsuccessful in optimizing the conversion process for thick PVD- BaF_2 films on IBAD MgO.

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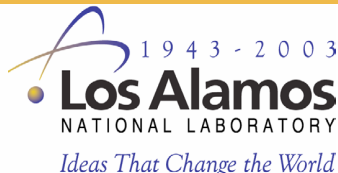
FY2004 Plans (Scoring Criterion)

- ➔ Determine by how much the established baseline $J_c(d)$ can be improved upon with an optimized PVD-BaF₂ process.
 - ✓ Produce films on single crystal substrates up to 5 μm with optimized process.
 - ✓ Spatially correlate the through-thickness J_c determined by ion milling with the microstructure for films grown with the modified process
- ➔ Investigate the initial stages of liquid phase formation and YBCO precipitation at different rates of the conversion process.
 - ✓ Determine the liquid phase composition
 - ✓ Determine the reaction sequence to form Y-123.
 - ✓ Obtain 10Å/s growth rate with PVD BaF₂

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FY2004 Plans (Scoring Criterion)

- ➔ Develop a compatible buffer layer architecture for the PVD BaF₂ process on the IBAD-MgO template.
 - ✓ Investigate the morphology of intermediate buffer layers and propagation of epitaxy and roughness through the buffer layer stack
 - ✓ Research to be led by LANL, performed at LANL and ORNL
 - ✓ Grow YBCO films of various thickness on qualified buffer layer stacks

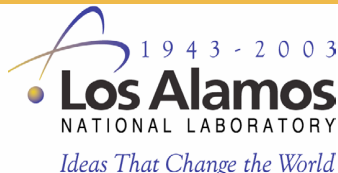
- ➔ Correlate the microstructure and through-thickness J_c on partially and fully converted MOD BaF₂ YBCO films and compare the results to PVD BaF₂ YBCO films.

- ➔ Increase I_c in PVD BaF₂ YBCO films on CC substrates to values > 400 A/cm-width (77 K).

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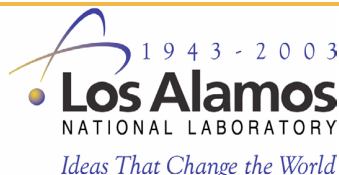
Research Integration (Scoring Criterion)

- ➔ This research group represents an synergistic effort between two national labs, a leading university research group, and an industry leader in coated conductor research and development.
- ➔ Each partner brings unique expertise to the collaboration.
- ➔ Focused support of American Superconductor in its effort to commercialize coated conductors using the ex-situ YBCO process.
- ➔ Multiple interactions at the individual level further leverage the research
 - ✓ NIST-Gaithersburg (phase development) and NIST-Boulder (strain effects)
 - ✓ ANL (Raman spectroscopy)
 - ✓ SNL (Buffer layers)
 - ✓ Collaboration / Information exchange with Stanford University and other participants of the MURI project
 - ✓ Institute de Ciencia de Materials de Barcelona, Spain (granularity effects)
 - ✓ Kyushu University, Japan ($J_c(H,T)$)

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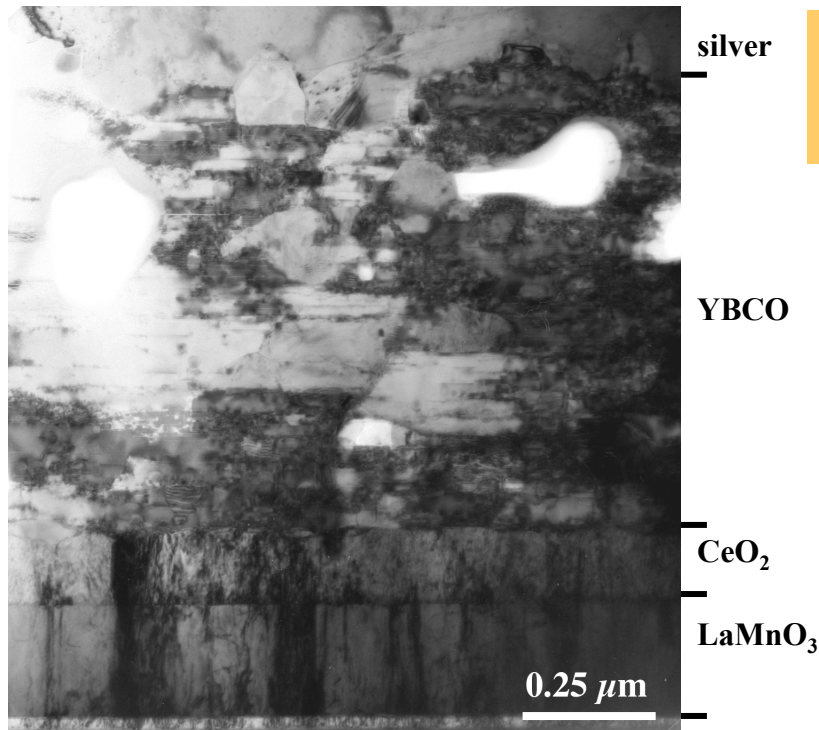
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High- J_c , I_c films were obtained on IBAD MgO by MOD-BaF₂ at AMSC; PVD-BaF₂ *ex-situ* processing has not yet been optimized for reproducible results.

- The “single-crystal-like” textures obtained in IBAD MgO templates provides a compelling reason to continue working with them. (See Paul Arendt and Steve Foltyn-Friday 8:30 a.m.)
- The YBCO grain size is the same on all substrates. (process, not substrate dependent).



AMSC YBCO / ORNL LaMnO₃ / LANL IBAD MgO
MOD-BaF₂ YBCO / CeO₂ / LaMnO₃ / IBAD MgO
 $t(\text{YBCO}) = 0.89 \mu\text{m}$ -- $J_c(170\text{A/cm-width}, 77\text{K}) = 1.9 \text{ MA/cm}^2$

PVD-BaF₂ results with MgO and IBAD MgO

PVD-BaF₂ YBCO / LaMnO₃ / single crystal MgO
 $t(\text{YBCO}) = 0.3 \mu\text{m}$; $J_c(77\text{K}, \text{SF}) = 4.4 \text{ MA/cm}^2$

PVD-BaF₂ YBCO / LaMnO₃ / IBAD MgO
 $t(\text{YBCO}) = 0.3 \mu\text{m}$; $J_c(77\text{K}, \text{SF}) = 2.2 \text{ MA/cm}^2$